EP0118657

Publication Title:

Non-aqueous electrochemical cell.

Abstract:

A non-aqueous electrochemical cell has an anode (2) consisting of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (3) consisting of a porous carbon body (7) and a current collector (6); and an electrolyte containing an oxyhalide, wherein the porous carbon body (7) contains a carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on a surface of each of carbon black particles. The cell has a high discharge capacity and an excellent discharge efficiency in high rate discharge.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 118 657**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 84100066.4

(22) Date of filing: 04.01.84

(51) Int. Cl.³: H 01 M 6/14
H 01 M 4/96, H 01 M 4/40

(30) Priority: 14.01.83 JP 4537/83
14.01.83 JP 4538/83
17.03.83 JP 45123/83
19.07.83 JP 130154/83
19.07.83 JP 130155/83
22.09.83 JP 146968/83 U
22.09.83 JP 146969/83 U

(43) Date of publication of application:
19.09.84 Bulletin 84/38

(84) Designated Contracting States:
DE FR GB

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(54) **Non-aqueous electrochemical cell.**

(57) A non-aqueous electrochemical cell has an anode (2) consisting of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (3) consisting of a porous carbon body (7) and a current collector (6); and an electrolyte containing an oxyhalide, wherein the porous carbon body (7) contains a carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on a surface of each of carbon black particles. The cell has a high discharge capacity and an excellent discharge efficiency in high rate discharge.

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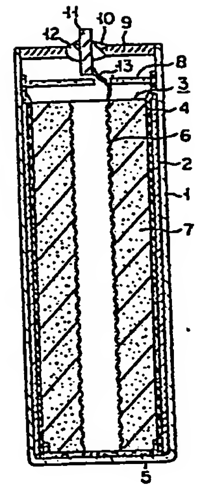


Non-aqueous electrochemical cell

The present invention relates to an improvement in a non-aqueous electrochemical cell.

A non-aqueous electrochemical cell using lithium or sodium as an active anode material has high energy density, good storage characteristics, and wide operation temperature range. A non-aqueous electrochemical cell is therefore often used as a power source for a calculator, a watch, or a memory backup system. Such a cell comprises an anode, an electrolyte and a cathode. In general, such a cell uses as an anode an alkali metal such as lithium or sodium; as an electrolyte or electrolytic solution, a solution of a solute such as lithium perchlorate or lithium tetrafluoroborate in a non-aqueous solvent such as propylene carbonate, γ-butyrolactone, or dimethoxyethane; and as a cathode, manganese dioxide or poly-carbonmonofluoride.

Among such cells, a cell using thionyl chloride as a main active cathode material is receiving a lot of attention due to its high energy density. A cell of this type has a cathode consisting of a porous carbon body and a current collector and has an electrolyte, a solution of lithium chloride ($LiC\ell$) and aluminum chloride ($A\ell C\ell_3$) in thionyl chloride ($SOC\ell_2$). Therefore, $SOC\ell_2$ serves both as the main active cathode material and as the solvent for the electrolyte salt.

In a cell using $SOC\ell_2$ as an active cathode material, the anode reaction is the reaction in which the anode metal is dissolved in the electrolyte as metal ions. On the other hand, the cathode reaction occurs on the porous carbon body as one constituent member of the cathode, and the reaction product of the cathode reaction is deposited on the porous carbon body. However, in a conventional cell having a cathode comprising a porous carbon body which is obtained by mixing acetylene black with a polymer binder such as polytetrafluoroethylene, forming a resultant mixture into a predetermined shape, and drying the formed body upon deposition of the reaction product on the porous carbon body, the electrode reaction is significantly interfered with and the discharge capacity is lowered. Especially, the discharge efficiency is considerably lowered in a high rate discharge as compared to a low rate discharge.

The cell described above uses an oxyhalide such as thionyl chloride, which is highly corrosive, as a main active cathode material. For this reason, the cell container must be sealed so that the oxyhalide may not leak outside the container and may not corrode equipment in which the cell is mounted. The oxyhalide is in the liquid form and is highly volatile. Accordingly, from the viewpoint of the working environment for manufacturing such cells and the viewpoint of the cell characteristics, an electrolyte containing such an oxyhalide must be injected and held in a cell container after cell constituent elements (anode, separator, and cathode) are placed inside the container.

In view of the foregoing, a cell assembly method to be described below has been proposed. According to this method, cell constituent elements consisting of an anode, a separator and a cathode are placed in a metal can. A metal top is prepared by liquid-tightly sealing, an injection metal pipe serving as one polarity terminal

through a sealing material such as a glass or a ceramic. The metal top is fitted in the open upper end of the metal can and is sealed by laser welding or the like. Then, an electrolyte containing an oxyhalide is injected into the metal can through the metal pipe. A metal needle is inserted into the metal pipe, and the pipe and the upper end of the needle are liquid-tightly sealed by laser welding or the like. However, in this method, when the upper portion of the metal pipe and the upper end of the metal needle are welded, the electrolyte attached to the inner circumferential surface of the pipe or near the lower end of the pipe is evaporated due to the heat of welding, and is introduced between the pipe and the needle in the form of gas. This gives rise to defective welding (pinholes in many cases) and a lower yield of cells.

It is an object of the present invention to provide a non-aqueous electrochemical cell which has a high discharge capacity and an excellent discharge efficiency in a high rate discharge.

It is another object of the present invention to provide a non-aqueous electrochemical cell which has a high discharge capacity and an excellent discharge efficiency in a high rate discharge, and which has a cathode comprising a porous carbon body having a good size stability.

It is still another object of the present invention to provide a non-aqueous electrochemical cell in which defective sealing of a metal pipe for electrolyte injection which also serves as one polarity terminal and which is liquid-tightly sealed to a metal top is reduced to the minimum.

According to an aspect of the present invention, there is provided a non-aqueous electrochemical cell comprising an anode consisting of an element selected from the group consisting of lithium, sodium and aluminum; a cathode consisting of a porous carbon body

and a current collector; and an electrolyte containing an oxyhalide, wherein the porous carbon body contains carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on a surface of each of carbon black particles.

The porous carbon body can further contain acetylene black.

According to another aspect of the present invention, there is provided a non-aqueous electrochemical cell comprising an anode consisting of an element selected from the group consisting of lithium, sodium and aluminum; a cathode consisting of a porous carbon body and a current collector; and an electrolyte containing an oxyhalide, wherein the porous carbon body has a porosity of 70 to 85%, and the volume of pores having a pore size of 0.1 to 2 μm comprise 30% or more of all pore volume.

According to still another aspect of the present invention, there is provided a non-aqueous electrochemical cell comprising a metal can serving also as one polarity terminal; an anode which is housed in said metal can and which consists of an element selected from the group consisting of lithium, sodium and aluminum; a cathode which is housed in said metal can and which consists of a porous carbon body and a current collector; a separator for physically separating said anode and said cathode in said metal can; metal top hermetically sealed to an open upper end of said metal can; a metal pipe which is inserted in said metal top and which also serves as the other polarity terminal; an electrolyte which contains an oxyhalide and which is introduced into said metal can through said metal pipe; and means for sealing said pipe, wherein a level of the electrolyte contained in said metal can is lower than a lower end of said metal pipe which is in said metal can.

According to still another aspect of the present invention, there is provided a non-aqueous

electrochemical cell comprising a metal can serving also as one polarity terminal; an anode which is housed in said metal can and which consists of an element selected from the group consisting of lithium, sodium and aluminum; a cathode which is housed in said metal can and which consists of a porous carbon body and a current collector; a separator which physically separates said anode and said cathode in said metal can; metal top hermetically sealed to an open upper end of said metal can, said metal top having a central portion made of insulating material; a metal pipe which is extends into said metal can through the central portion of said metal top and which also serves as the other polarity terminal; an electrolyte which contains an oxyhalide and which is injected into said metal can through said metal pipe; and a metal plug inserted in said metal pipe, wherein a portion of said metal pipe through which said metal plug is inserted is caulked, and an upper end of the portion of said metal pipe and said metal plug are welded together.

In this cell, the metal plug can have at its upper end a flange which abuts against the upper end face of the metal pipe, the portion of the metal pipe through which the metal plug is inserted is caulked, and an upper end of the metal pipe and the metal plug are welded together.

In this cell, the metal plug can have at its upper end a flange which abuts against the upper end face of the metal pipe, and at part of its outer circumferential surface a bulged portion which abuts against the inner circumferential surface of the metal pipe.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a cross-sectional view of a lithium-thionyl chloride cell according to Example 1 of the present invention;

Fig. 2 is a graph showing the relationship between the terminal voltage and discharge time in a cell of Example 1 and Comparative Example 1;

Fig. 3 is a cross-sectional view showing a lithium-thionyl chloride cell according to Example 2 of the present invention;

Fig. 4 is a graph showing the relationship between the terminal voltage and discharge time of cells of Examples 2 and 3 and Comparative Example 2;

Fig. 5 is a cross-sectional view showing a lithium-thionyl chloride cell according to Example 4 of the present invention;

Fig. 6 is a graph showing the relationship between the discharge capacity and discharge current in a cell of Examples 4 and 5 and Comparative Example 3;

Figs. 7 and 8 are respectively cross-sectional views of lithium-thionyl chloride cells according to Examples 6 and 7 of the present invention;

Fig. 9 is a cross-sectional view showing a lithium-thionyl chloride cell according to Example 8 of the present invention;

Fig. 10 is a front view of a metal plug having a flange at its upper end, which is used in the cell shown in Fig. 9;

Fig. 11 is a cross-sectional view of a lithium-thionyl chloride cell according to Example 9 of the present invention;

Fig. 12 is a cross-sectional view of a metal plug which has a flange at its upper end and a bulged portion at the center of its outer circumferential surface and which is used in the cell shown in Fig. 11; and

Figs. 13 and 14 are cross-sectional views of metal plugs which are used in modifications of Example 9, respectively, of the present invention.

Of various types of carbon materials, a carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on the surface of each of

carbon black particles has an extremely high conductivity and an extremely great specific surface area. Based on this fact, the present inventors have found that when a cathode consisting of a current collector and a porous carbon body containing such a carbon black as a main component is used, a non-aqueous electrochemical cell having excellent discharge characteristics can be obtained.

The cathode as described above can be obtained in the following manner. A polymer binder such as polytetrafluoroethylene is added to the carbon black as described above. After adding an organic solvent such as ethyl alcohol, the resultant mixture is agitated and milled well. The milled substance is applied on a current collector of a metal net, a punched metal, or an expanded metal and is dried thereafter. When the porous carbon body containing as a main component a mixture of the carbon black having a special structure as described above and acetylene black is used, a non-aqueous electrochemical cell which has high discharge capacity and high discharge efficiency in high rate discharge and which has excellent size stability is obtained.

Regarding the mixing ratio of the carbon black having a thin layer of graphite crystals on the surface of each particle and the acetylene black, it is preferable that the carbon black is used in an amount of 20 to 80% by weight and the acetylene black is used in an amount of 80 to 20% by weight.

In a cell according to a first aspect of the present invention, the porosity of the porous carbon body is limited to fall within a predetermined range for the following reasons. When the porosity of the porous carbon body is less than 70%, the reaction efficiency is degraded. On the other hand, when the porosity of the porous carbon body exceeds 85%, the strength of the porous carbon body is degraded. The pore size of pores of the porous carbon body is defined to fall within a

predetermined range for the following reasons. When the pore size is less than 0.1 μm, the pores become clogged by the reaction product of the thionyl chloride as an active cathode material. On the other hand, when the pore size exceeds 2 μm, the reaction area of the porous carbon body is decreased, resulting in a degradation in the reaction efficiency. The ratio of the volume of pores having a pore size of 0.1 to 2 μm to the total volume of pores is limited to fall within a predetermined ratio for the following reason. When the ratio is less than 30%, the reaction efficiency cannot be increased satisfactorily.

Example 1

The present invention will now be described with reference to a case of a lithium-thionyl chloride cell.

Fig. 1 shows a cross-sectional view of a cell of R03 size. Referring to Fig. 1, reference numeral 1 denotes a metal can (10 mm outer diameter, 42 mm height) of stainless steel which also serves as an anode terminal and which has an open upper end. A cylindrical anode 2 of metal lithium (0.6 mm thickness) is fitted inside the metal can 1. A cathode 3 is arranged inside a glass fiber separator 4 which is arranged inside the anode 2. An insulating sheet 5 is interposed between the bottom surfaces of the cathode 3 and the metal can 1. The cathode 3 consists of a current collector 6 of a stainless steel net and a cylindrical porous carbon body 7. The cathode 3 is prepared by mixing 90% by weight of a carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on the surface of each of carbon black particles ("Ketjenblack EC": Trade name of Lion Akzo Co., Inc.) and 10% by weight of polytetrafluoroethylene; adding ethanol to the mixture; milling the mixture; forming the milled substance into a cylidrical shape (8 mm outer diameter, 3 mm inner diameter, and 35 mm height) such that the current collector faces inward; and drying the

assembly in vacuo at 150°C. Thus, the cathode 3 is obtained wherein the cylindrical porous carbon body 7 is formed around the current collector 6.

An insulating layer sheet 8 is supported by the separator 4 to be above the cathode 3 inside the can 1. A metal top 9 is sealed to the open upper end of the can 1 by laser welding or the like. A hole 10 is formed at the center of the metal top 9. An electrolyte comprising a 1.8 mol/ℓ solution of lithium tetrachloro-aluminate ($LiA\ell C\ell_4$) in thionyl chloride ($SOC\ell_2$) is injected into the metal can 1 through the hole 10. A cathode terminal 11 is fixed in the hole 10 of the metal top 9 by means of a metal-glass sealing material 12 and is electrically insulated from the metal top 9. The cathode terminal 11 is connected to the current collector 6 of the cathode 3 by a lead wire 13 mounted at the lower end of the terminal 11.

Comparative Example 1

A lithium-thionyl chloride cell of R03 size having the same structure as that of Example 1 was prepared following the same procedures as in Example 1 except that acetylene black was used as carbon black.

The cells of Example 1 and Comparative Example 1 were examined for their characteristic of 300 Ω constant load discharge at room temperature. The characteristic curves as shown in Fig. 2 were obtained. Curve A in Fig. 2 is a discharge characteristic curve of the cell of Example 1 and curve B shows the same of the cell of Comparative Example 1. As may be apparent from Fig. 2, the cell (curve A) of Example 1 has significantly longer discharge time than that (cell B) of Comparative Example 1 and higher discharge voltage than that of Comparative Example 1. The cell of Example 1 of the present invention is assumed to provide such good discharge characteristics for the following reason. The porous carbon body of the cathode contains as its main component a carbon black in which a thin layer of

graphite crystals is formed on the surface of each of chain-like particles. Therefore, the conductivity and the reaction surface area of the cathode are considerably improved.

In Example 1 above, a cylindrical cathode is used. However, the present invention is not limited to this. For example, a milled substance of a carbon black and a polymer binder may be applied on a metal current collector to provide a belt-like electrode, and the belt-like electrode can be wound and dried to provide a spiral cathode.

Example 2

Fig. 3 shows a cross-sectional view of a cell of R6 size. Referring to Fig. 3, reference numeral 21 denotes a metal can (14 mm outer diameter, 47 mm height) of stainless steel, which also serves as an anode terminal, and which has an open upper end. A cylindrical anode 22 of metal lithium (0.75 mm thickness) is applied on the inner circumferential surface of the metal can 21. A cathode 23 is arranged inside a glass fiber separator 24. An insulating sheet 25 is interposed between the bottom surfaces of the cathode 23 and the metal can 21.

The cathode 23 is prepared by the following method. A mixture is prepared by mixing 45% by weight of a carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on the surface of each of carbon black particles ("Ketjenblack EC": Trade name, Lion Akzo Co., Inc.), 45% by weight of acetylene black, and 10% by weight of a powder of polytetrafluoroethylene; adding ethanol to the resulant mixture in a ratio of 8 mℓ per gram of the mixture; and sufficiently milling the mixture. The milled substance is formed into a cylindrical shape (10 mm outer diameter, 6 mm inner diameter, and 38 mm height) together with a current collector 26 comprising a nickel net such that the current collector 26 faces inward. The formed body is dried in vacuo at 200°C to provide

the cathode 23 wherein a cylindrical porous carbon body 27 is applied on the outer circumferential surface of the current collector 26.

An insulating paper sheet 28 with a hole is supported by the separator 24 to be located above the cathode 23 in the metal can 21. A metal top 29 is sealed to the open upper end of the metal can 21 by laser welding or the like. A hole 30 is formed at the center of the metal top 29. An electrolyte comprising a 1.8 mol/ℓ solution of lithium tetrachloroaluminate ($LiA\ell C\ell_4$) in thionyl chloride ($SOC\ell_2$) is injected into the metal can 21 through the hole 30 of the metal top 29. A cathode terminal 31 is fixed in the hole 30 of the metal top 29 by means of a metal-glass sealing material 32 and is electrically insulated from the metal top 29. The lower end of the cathode terminal 31 is connected to the current collector 26 of the cathode 23 by a lead wire 13.

Example 3

A lithium-thionyl chloride cell of R6 size having the same structure as that of Example 1 was assembled using the same cathode as that in Example 1 except that a mixture used consisted of 25% by weight of "Ketjenblack EC" (Lion Akzo Co., Inc.), 65% by weight of acetylene black, and 10% by weight of a powder of polytetrafluoroethylene.

Comparative Example 2

A lithium-thionyl chloride cell of R6 size having the same structure as that of Example 1 was assembled using a cathode as in Example 1 except that a mixture used consisted of 90% by weight of acetylene black and 10% by weight of a powder of polytetrafluoroethylene.

One hundred, each, of the cells of Examples 2 and 3 and Comparative Example 2 were prepared. The diameters of these cells before and after drying were measured, and the results as shown in the Table below were obtained. The Table also shows the number of cathodes

which exhibited separation or peeling off of the porous carbon body from the current collector and the number of cathodes which could not be inserted into metal cans due to expansion of the porous carbon body.

Table

	Average cathode diameter (mm)		Number of cathodes prepared		
	Before drying	After drying	No. of satisfactory cathodes	No. of unsatisfactory cathodes: Separation of porous carbon body	No. of unsatisfactory cathodes: Could not be inserted into metal can
Example 2	10	10	99	1	0
Example 3	10	10.2	100	0	0
Comparative Example 2	10	11	86	0	14

As may be seen from the Table above, the cathodes of the cells of Examples 2 and 3 indicate only small changes in size and are rarely susceptible to the problems of a defective porous carbon body or the impossibility of inserting the cathode into a metal can due to expansion of the porous carbon body. In contrast to this, a number of cathodes in the cells of Comparative Example 2 suffered significant variations in size after drying and could not be inserted into metal cans.

Cells of Examples 2 and 3 and Comparative Example 2 were examined for their characteristics of 300 Ω load discharge at room temperature. Fig. 4 shows the obtained characteristics. Referring to Fig. 4, curve A represents a discharge characteristic curve of the cell of Example 2, curve B represents the same of the cell of Example 3, and curve C represents the same of the cell of Comparative Example 2. As may be seen from Fig. 4, the cells of Examples 2 and 3 have longer discharge time and higher discharge voltage than those of the cell (Comparative Example 2) having a cathode comprising a porous carbon body containing acetylene black alone as a main component.

Example 4

After adding polytetrafluoroethylene in an amount of 10% by weight to a mixture consisting of 45% by weight of acetylene black and 45% by weight of "Ketjenblack EC" (Lion Akzo Co., Ltd.) having an average particle size of 40 mμm and a DBP absorption of 200 cm^3/100g, ethanol was added to the resultant mixture and milling was performed. As shown in Fig. 5, the milled substance was formed into a cylindrical body (10.5 mm outer diameter, 5 mm inner diameter, and 38 mm height) together with a current collector 47 comprising a stainless steel net such that the current collector 47 faces inward. The cylindrical body was dried in vacuo at 150°C. Thus, a cathode 43 was obtained in which a

cylindrical porous carbon body 46 was adhered to the outer circumferential surface of the current collector 47. The porous carbon body 46 of the cathode 43 had a porosity of 80%. When the pore distribution of the porous carbon body 46 was examined by the mercury injection method, 37% of the total pore volume is found to be consisted by the pores having a diameter falling within the range of 0.1 to 2 μm. Subsequently, the cathode 43 was arranged inside a separator 44 in a metal can 41 of stainless steel having an outer diameter of 14 mm and a height of 47 mm, in which a cylindrical anode 42 having a thickness of 0.7 mm and consisting of metal lithium was adhered to the inner circumferential surface thereof. After assembling an insulating paper sheet 48 and sealing the metal can 41 with a metal top 49, an electrolyte was injected into the metal can 41 through a hole 50 formed in the metal top 49. The electrolyte consisted of a 1.8 mol/ℓ solution of lithium tetrachloroaluminate ($LiA\ell C\ell_4$) in thionyl chloride ($SOC\ell_2$). A cathode 51 connected to the current collector 47 through a lead wire 53 was fixed in the hole 50 of the metal top 49 by means of a sealing material 52. A lithium-thionyl chloride cell of R6 size was thus assembled as shown in Fig. 5. In Fig. 5, reference numeral 45 denotes an insulating paper sheet interposed between the bottom surfaces of the cathode 43 and the metal can 41.

Example 5

A cathode was prepared using a carbon black ("VULCAN XC-72R" available from Cabot Corp.) having an average particle size of 30 mμm and a DBP oil absorption of 185 cm^3/100g, following the same procedures as in Example 4. The porous carbon body of the cathode had a porosity of 82%, and the volume of pores having a pore size of 0.1 to 2 μm comprised 34% of the total pore volume. Using this cathode, a lithium-thionyl chloride cell as shown in Fig. 5 was assembled following the same

procedures as in Example 4.

Comparative Example 3

A cathode was prepared using a carbon black ("ELFTEX 8" available from Cabot Corp.) having an average particle size of 30 mμm and a DBP oil absorption of 100 $cm^3/100g$, following the same procedures as in Example 4. Using this cathode, a lithium-thionyl chloride cell having the same structure as shown in Fig. 5 was assembled. The porous carbon body of the cathode had a porosity of 84%, and the volume of pores having a pore size of 0.1 to 2 μm had 24% of the total pore volume.

The cells of Examples 4 and 5 and Comparative Example 3 were examined for the relationship between the discharge current and discharge capacity to end voltage of 2.5 V. The characteristics as shown in Fig. 6 were obtained. Referring to Fig. 6, curve A represents the discharge current vs. discharge capacity characteristics of the cell of Example 4, curve B represents the same of the cell of Example 5, and curve C represents the same of the cell of Comparative Example 3. As may be seen from Fig. 6, the cells of the present invention (curves A and B) have substantially an equivalent discharge capacity to that of the conventional cell (curve C) in low rate discharge but have an extremely higher discharge capacity in high rate discharge.

Example 6

As shown in Fig. 7, a stainless steel metal can 61 was prepared which had an outer diameter of 14 mm, a height of 47 mm and a thickness of 0.3 mm, which had an open upper end, and which also served as an anode terminal. A cylindrical anode 62 having a thickness of 0.7 mm and consisting of metal lithium was placed inside the metal can 61.

A cathode 63 was placed inside a cylindrical glass fiber separator 64. The cathode 63 was prepared by the following method. A dispersion of

polytetrafluoroethylene (binder) was added in an amount (in terms of polytetrafluoroethylene) of 10% by weight to a mixture of 45% by weight of "Ketjenblack EC" available from Lion Akzo Co., Inc. and 45% by weight of acetylene black. The mixture was milled, and formed to provide a cylindrical porous carbon body 65 having an outer diameter of 12 mm, an inner diameter of 5 mm, and a height of 40 mm. A cylindrical current collector 66 consisting of nickel expanded metal was placed inside the porous carbon body 65. An insulating sheet 67 was supported by the separator 64 above the cathode 63 in the metal can 61.

A metal top 71 was prepared which had a hole 68 at its center for receiving a stainless steel pipe 70 as a cathode terminal by a glass sealing material 69. After connecting the pipe 70 to the current collector 66 of the cathode 63 housed in the metal can 61 by a nickel lead wire 72, the metal top 71 was hermetically sealed to the open upper end of the metal can 61 by laser welding. Thereafter, 3.5 mℓ of a 1.8 mol/ℓ solution (electrolyte) 73 of lithium tetrachloroaluminate ($LiA\ell C\ell_4$) in thionyl chloride were injected into the metal can 61 through the pipe 70 such that the electrolyte 73 was contained in the metal can 61 to the level lower than the lower end of the pipe 70. A sealing needle 74 was inserted into the pipe 70, and the pipe 70 and the needle 74 were welded by laser welding to seal the pipe 70. A lithium-thionyl chloride cell was thus prepared.

Comparative Example 4

A lithium-thionyl chloride cell was prepared following the same procedures as in Example 6 except that after sealing a metal top to an open upper end of a metal can, 4.3 mℓ of a 1.8 mol/ℓ solution (electrolyte) of lithium tetrachloroaluminate in thionyl chloride were injected into the metal can through a stainless steel pipe to the level higher than the lower end of the

stainless steel pipe.

One thousand cells of each of Example 6 and Comparative Example 4 were prepared. The obtained cells were tested by means of a helium leak detector to determine the number of cells in which the stainless steel pipes were not satisfactorily sealed. The results as shown in the Table below were obtained.

Table

	Number of unsatisfactorily sealed cells per 1,000 cells
Example 6	18
Comparative Example 4	56

As may be seen from the above Table, when the electrolyte is contained in the metal can to the level lower than the lower end of the stainless steel pipe, the rate of occurrence of unsatisfactory sealing can be considerably reduced. Furthermore, when the pipe is sealed by laser welding, generation of a mist of the electrolyte can be prevented, so that the working environment is not contaminated and the manufacturing apparatus is not damaged.

In Example 6, before the electrolyte is injected into a metal can to the level lower than the lower end of a metal pipe, the volume of the metal can housing the cathode therein is measured, and the proper amount of electrolyte is injected into the metal can. However, the present invention is not limited to this. For example, the electrolyte can be injected into a metal can to the level lower than the lower end of a metal pipe by roughly estimating the volume of a metal can, injecting a corresponding amount of electrolyte into the metal can, and heating the metal can so as to spill off any extra amount of electrolyte (corresponding to the electrolyte portion above the lower end of the metal

pipe) through the metal pipe.

In Example 6, the metal pipe is sealed by inserting a pin into the metal pipe and laser welding the pin and the metal pipe. However, the present invention is not limited to this. For example, the metal pipe can be directly laser welded without inserting a pin therein. Furthermore, welding is not limited to laser welding and can be electric welding or arc welding.

Example 7

Example 7 will now be described with reference to Fig. 8.

Referring to Fig. 8, reference numeral 81 denotes a metal can of stainless steel, which also serves as an anode terminal. A cylindrical anode 82 consisting of metal lithium is adhered to the inner circumferential surface of the metal can 81. A cathode 83 is housed inside separators 84a and 84b which comprise glass fiber nonwoven fabrics and which are arranged inside the inner circumferential surface of the anode 82 and the inner bottom surface of the metal can 81. The cathode 83 is prepared by the following method. A dispersion of a commercially available polytetrafluoroethylene is added in an amount of 10% by weight (in terms of the amount of the polytetrafluoroethylene) to a mixture of acetylene black and "Ketjenblack EC". After adding water and ethyl alcohol to the resultant mixture, the mixture is agitated at room temperature for about 2 hours and thereafter milled. The milled substance is formed into a cylindrical shape together with a current collector 85 comprising a stainless steel net such that the current collector 85 faces inward. The obtained cylindrical body is dried in vacuo at 200°C. Thus, the cathode 83 is obtained in which a cylindrical porous carbon body 86 is adhered on the outer surface of the current collector 85.

An insulating sheet 87 having a central hole and supported by the separator 84a is arranged above the

cathode 83 inside the metal can 81. A metal top 88 is sealed to the open upper end of the metal can 81 by laser welding or the like. The metal top 88 has a hole 89 at its center. A stainless steel pipe 90 is fixed in the hole 89 by a metal-glass sealing material 91. The lower end of the pipe 90 is connected to the current collector 85 of the cathode 83 through a lead wire 92. A 1.5 mol/ℓ solution (electrolyte) 93 of lithium tetrachloroaluminate ($LiA\ell C\ell_4$) in thionyl chloride is injected into the metal can 81 through the pipe 90, to be held in the metal can 81. After injecting the electrolyte 93, a stainless steel needle 94 is inserted into the stainless steel pipe 90. An annular narrowed portion 95 narrowed toward the needle 94 is formed by caulking that portion of the pipe 90 which projects upward from the top surface of the metal top 88. The upper end of the pipe 90 above the narrowed portion 95 and the needle 94 are welded together by laser welding.

With the above structure, before the stainless steel pipe 90 serving also as a cathode terminal and the stainless steel needle 94 are welded together for sealing, the narrowed portion 95 is formed in the pipe 90 to achieve temporary sealing. Thus, this narrowed portion 95 serves to prevent leakage of the electrolyte in either gaseous or liquid form to the welding portion between the upper end of the pipe 90 and the upper portion of the needle 94 due to a temperature increase during welding. For this reason, since no electrolyte or the like is present between the upper end of the pipe 90 and the upper portion of the needle 94 to be welded together, welding can be performed excellently by laser welding without pin holes or the like being formed.

One hundred cells were assembled for each of Example 7 and conventional cells prepared without caulking before sealing. The cells were examined by a microscope (x20) to determine the number of cells having pin holes after sealing. Twenty-three conventional

cells suffered defective welding, while no cell of Example 7 suffered defective welding.

Example 8

Example 8 will now be described with reference to Figs. 9 and 10.

Referring to Figs. 9 and 10, reference numeral 101 denotes a metal can of stainless steel serving also as an anode terminal. A cylindrical anode 102 of metal lithium is adhered on the inner circumferential surface of the metal can 101. A cathode 103 is housed inside separators 104a and 104b comprising glass fiber nonwoven fabric which are respectively arranged on the inner circumferential surface of the anode 102 and the inner bottom surface of the metal can 101. The cathode 103 is prepared by the following method. A dispersion of a commercially available polytetrafluoroethylene is added in an amount of 10% by weight (in terms of the amount of polytetrafluoroethylene) to a mixture of acetylene black and "Ketjenblack EC". After adding water and ethyl alcohol to the mixture, the resultant mixture is agitated at room temperature for 2 hours, and milled. The milled substance is formed into a cylindrical shape together with a current collector 105 comprising a stainless steel net such that the current collector 105 faces inward. The formed body is dried in vacuo at 200°C. Thus, the cathode 103 in which a cylindrical porous carbon body 106 is adhered on the outer circumferential surface of the current collector 105 is obtained.

An insulating paper sheet 107 having a central hole is supported by the separator 104a above the cathode 103 inside the metal can 101. A metal top 108 of stainless steel is sealed to the open upper end of the metal can 101 by laser welding or the like. A hole 109 is formed at the center of the metal top 108. A stainless steel pipe 110 serving also as a cathode terminal is fixed in the hole 109 through a metal-glass sealing material 111.

The lower end of the pipe 110 is connected to the current collector 105 of the cathode 103 by a lead wire 112. A 1.5 mol/ℓ solution (electrolyte) 113 of lithium tetrachloroaluminate ($LiA\ell C\ell_4$) in thionyl chloride is injected into the metal can 101 through the pipe 110. After the electrolyte 113 is injected into the metal can 101, a stainless steel needle 115 having a flange 114 of a diameter equal to that of the outer diameter of the pipe 110, as shown in Fig. 10, is inserted in the pipe 110 such that the flange 114 of the needle 115 abuts against the upper end face of the pipe 110. An annular narrowed portion 116 is formed by caulking to narrow toward the needle 115 at that portion of the pipe 110 which extends outside the metal top 108. The upper end face of the pipe 110 and the flange 114 of the needle 115 are sealed together by laser welding.

With the above structure, before the pipe 110 serving also as the cathode terminal and the needle 115 are sealed together, the annular narrowed portion 116 is formed in the pipe 110 by caulking to achieve temporary sealing. Accordingly, the narrowed portion 116 serves to prevent upward leakage of the electrolyte 113 in the metal can 101 in either gaseous or liquid form toward the upper end of the pipe 110 due to a temperature increase during welding. Even if the electrolyte 113 leaks through the narrowed portion 116, the flange 114 at the upper end of the needle 115 abuts against the upper end face of the pipe 110, so that any further leakage of the electrolyte is prevented. In this manner, since leakage of the electrolyte is prevented at two positions, i.e., the narrowed portion 116 and the lower surface of the flange 114, no electrolyte is presented between the upper end face of the pipe 110 and the flange 114 to be welded together. Thus, a non-aqueous electrochemical cell in which no pin holes are formed upon laser welding is obtained.

Two hundred cells were prepared for each of Example

8, Comparative Example 5 in which cells were obtained without caulking the stainless steel pipes before sealing, and Comparative Example 6 in which needles with no flange were used and the stainless steel pipes were caulked for sealing. The cells were tested for the presence of pinholes at the welded portions. The test was performed by counting the number of cells which exhibited white coloring at the welded portion after dripping a silver nitrate solution as a chlorine ion indicator onto this portion. As a result, in the cells of Comparative Example 5, 14 out of 200 cells exhibited white coloring. In the cells of Comparative Example 6, three out of 200 cells exhibited white coloring. In the cells of Example 8, no cell exhibited white coloring.

In Example 8, a needle had a flange of the same diameter as the outer diameter of the pipe. However, a needle having a flange of a diameter slightly smaller or larger than the outer diameter of the pipe may be used.

Example 9

Example 9 will now be described with reference to Figs. 11 to 14.

Referring to Figs. 11 to 14, reference numeral 121 denotes a metal can (stainless steel) serving also as an anode terminal. A cylindrical anode 122 of metal lithium is adhered on the inner circumferential surface of the metal can 121. A cathode 123 is housed inside separators 124a and 124b comprising glass fiber nonwoven fabrics which are respectively arranged on the inner circumferential surface of the anode 122 and the inner bottom surface of the metal can 121. The cathode 123 is prepared by the following method. A dispersion of a commercially available polytetrafluoroethylene is added in an amount of 10% by weight (in terms of the amount of the polytetrafluoroethylene) to a mixture of acetylene black and "Ketjenblack EC". After adding water and ethyl alcohol to the mixture, the resultant mixture is agitated at room temperature for about 2 hours, and is

milled. The milled substance is formed into a cylindrical shape together with a current collector 125 comprising a stainless steel net such that the current collector 125 faces inward. The cylindrical body obtained is dried in a vacuum at 200°C. As a result, the cathode 123 is prepared in which a porous carbon body 126 is formed around the outer circumferential surface of the current collector 125.

An insulating sheet 127 having a central hole is supported by the separator 124a above the cathode 123 in the metal can 121. A stainless steel top 128 is sealed at the open upper end of the metal can 121 by laser welding or the like. A hole 129 is formed at the center of the top 128. A stainless steel pipe 130 serving also as a cathode terminal is fixed in the hole 129 through a metal-glass sealing material 131. The lower end of the pipe 130 is connected to the current collector 125 of the cathode 123 by a lead wire 132. A 1.5 mol/ℓ solution (electrolyte) 133 of lithium tetrachloroaluminate ($LiA\ell C\ell_4$) in thionyl chloride is injected into the metal can 121 through the pipe 130. After the electrolyte 133 is injected into the metal can 121, a stainless steel stop 136 is inserted into the pipe 130. The stop 136 has, at its upper end, a flange 134 of a diameter slightly larger than the outer diameter of the pipe 130 and also has, on the outer surface near the lower end thereof, a spherical or bulb-like bulged portion 135, as shown in Fig. 12. The stop 136 is inserted into the pipe 130 such that the lower face of the flange 134 abuts against the upper end face of the pipe 130 and the bulged portion 135 abuts against the inner circumferential surface of the pipe 130. The diameter of the bulged portion 135 is set to be greater than the inner diameter of the pipe 130 by 1.02 mm. The upper end face of the pipe 130 and the abutting flange 134 of the stop 136 are sealed together by laser welding.

With the above structure, before the pipe 130

serving also as the cathode terminal and the stop 136 are sealed, the bulged portion 135 of the stop 136 abuts against the inner circumferential surface of the pipe 130 to achieve temporary sealing. Accordingly, leakage of the electrolyte toward the upper end of the pipe 130 due to an increase in temperature during laser welding is prevented by the tight contact between the inner circumferential surface of the pipe 130 and the bulged portion 135 of the stop 136. Even if the electrolyte leaks through this tight contact portion, the flange 134 abutting against the upper end face of the pipe 130 provides a good seal against any further leakage of the electrolyte. Thus, since the electrolyte is sealed at two positions, i.e., the tight contact portion as described above and the lower surface of the flange 134, no electrolyte is present between the upper end face of the pipe 130 and the flange 134. A non-aqueous electrochemical cell in which no pin holes are formed upon laser welding is obtained.

Two hundred cells were prepared for Example 9, Comparative Example 7 wherein cells were prepared using stops having no flange or bulged portion, and Comparative Example 8 wherein cells were prepared by using stops having only bulged portions on the outer circumferential surfaces thereof. The cells were tested for the presence of pinholes at the welded portions. The test was performed by counting the number of cells which exhibited white coloring at the welded portion after dripping a silver nitrate solution as a chlorine ion indicator onto the welded portion. In Comparative Example 7, 14 out of 200 cells exhibited white coloring. In Comparative Example 8, two out of 200 cells exhibited white coloring. In contrast to this, no cell exhibited white coloring in Example 9.

In Example 9, a stop having a flange of a diameter slightly larger than the outer diameter of the pipe was used. However, a stop having a flange of a diameter

equal to or slightly smaller than the outer diameter of the pipe can be used.

The diameter of the bulged portion of the stop is preferably larger than the inner diameter of the pipe by 1.01 to 1.03 mm. This is due to the following reason. When the diameter of the bulged portion exceeds that of the pipe by less than 1.01 mm, good adhesion between the bulged portion and the pipe inner circumferential surface is not obtained. On the other hand, when the diameter of the bulged portion of the stopper exceeds that of the pipe by more than 1.03 mm, the pipe may be damaged.

The shape of the metal stop is not limited to that described above. For example, a stop 136 having a bulb-like bulged portion 135 at its lower end as shown in Fig. 13 or a stop 136 having a conical bulged portion 135 at its lower end as shown in Fig. 14 may be used.

Claims:

1. A non-aqueous electrochemical cell comprising an anode (2) consisting of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (3) consisting of a porous carbon body (7) and a current collector (6); and an electrolyte containing an oxyhalide, wherein the porous carbon body (7) contains a carbon black having a chain-like structure wherein a thin layer of graphite crystals is formed on a surface of each of carbon black particles.

2. A cell according to claim 1, characterized in that the porous carbon body further contains acetylene black.

3. A cell according to claim 1, characterized in that the anode (2) consists of lithium.

4. A cell according to claim 1, characterized in that the oxyhalide is thionyl chloride.

5. A non-aqueous electrochemical cell comprising an anode (42) consisting of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (43) consisting of a porous carbon body (46) and a current collector (47); and an electrolyte containing an oxyhalide, wherein the porous carbon body has a porosity of 70 to 85% and the volume of pores having a pore size of 0.1 to 2 μm comprise not less than 30% of total pore volume.

6. A non-aqueous electrochemical cell comprising a metal can (61) serving also as one polarity terminal; an anode (62) which is housed in said metal can (61) and which consists of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (63) which is housed in said metal can (61) and which consists of a porous carbon body (65) and a current collector (66); a separator (64) for physically separating said anode (62) and said cathode (63) in said metal can (61); metal top (71) hermetically sealing an

open upper end of said metal can (61); a metal pipe (70) which is inserted in said metal top (71) and which also serves as the other polarity terminal; an electrolyte (73) which contains an oxyhalide and which is introduced into said metal can (61) through said metal pipe (70); and means (74) for sealing said pipe, wherein a level of the electrolyte contained in said metal can (61) is lower than a lower end of said metal pipe (70) which is in said metal can (61).

7. A non-aqueous electrochemical cell comprising a metal can (81) serving also as one polarity terminal; an anode (82) which is housed in said metal can (81) and which consists of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (83) which is housed in said metal can (81) and which consists of a porous carbon body (86) and a current collector (85); a separator (84a, 84b) which physically separates said anode (82) and said cathode (83) in said metal can (81); metal top (88) hermetically sealed to an open upper end of said metal can, said metal top having a central portion made of insulating material; a metal pipe (90) which extends into said metal can through the central portion of said metal top and which also serves as the other polarity terminal; an electrolyte (93) which contains an oxyhalide and which is injected into said metal can (81) through said metal pipe (90); and a metal plug (94) inserted in said metal pipe (90), wherein a portion of said metal pipe (90) through which said metal plug (94) is inserted is caulked, and an upper end of the portion of said metal pipe (90) and said metal plug (94) are welded together.

8. A non-aqueous electrochemical cell comprising a metal can (101) serving also as one polarity terminal; an anode (102) which is housed in said metal can (101) and which consists of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (103) which is housed in said metal can (101) and which

consists of a porous carbon body (106) and a current collector (105); a separator (104a, 104b) which physically separates said anode (102) and said cathode (103) in said metal can (101); metal top (108) hermetically sealed to an open upper end of said metal can, said metal top having a central portion made of insulating material; a metal pipe (110) which extends into said metal can through the central portion of said metal top and which also serves as the other polarity terminal; an electrolyte (113) which contains an oxyhalide and which is injected into said metal can (101) through said metal pipe (110); and a metal plug (115) inserted in said metal pipe (110), wherein said metal plug (115) has at an upper end thereof a flange (114) which abuts against an upper end face of said metal pipe (110), a portion of said metal pipe (110) through which said metal plug (115) is inserted is caulked, and an upper end of the portion of said metal pipe (110) and said metal plug (115) are welded together.

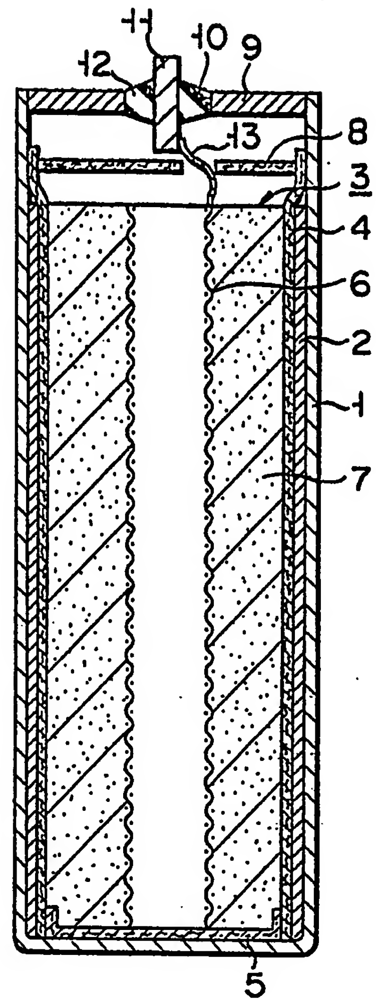
9. A non-aqueous electrochemical cell comprising a metal can (121) serving also as one polarity terminal; an anode (122) which is housed in said metal can (121) and which consists of an element selected from the group consisting of lithium, sodium and aluminum; a cathode (123) which is housed in said metal can (121) and which consists of a porous carbon body (126) and a current collector (125); a separator (124a, 124b) which physically separates said anode (122) and said cathode (123) in said metal can (121); metal top (128) hermetically sealed to an open upper end of said metal can, said metal top having a central portion made of insulating material; a metal pipe (130) which extends into said metal can through the central portion of said metal top and which also serves as the other polarity terminal; an electrolyte which contains an oxyhalide and which is injected into said metal can (121) through said

metal pipe (130); and a metal plug (136) inserted in said metal pipe (130), wherein said metal plug (136) has at an upper end thereof a flange (134) which abuts against an upper end face of said metal pipe (130) and at a part of an outer circumferential surface thereof a bulged portion (135) which abuts against an inner circumferential surface of said metal pipe (130).

10. A cell according to claim 9, characterized in that said bulged portion (135) of said metal plug (136) has a bulb-like shape.

11. A cell according to claim 9, characterized in that said bulged portion (135) of said metal plug (136) has a conical shape.

F I G. 1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10
9
12
13
8
3
4
6
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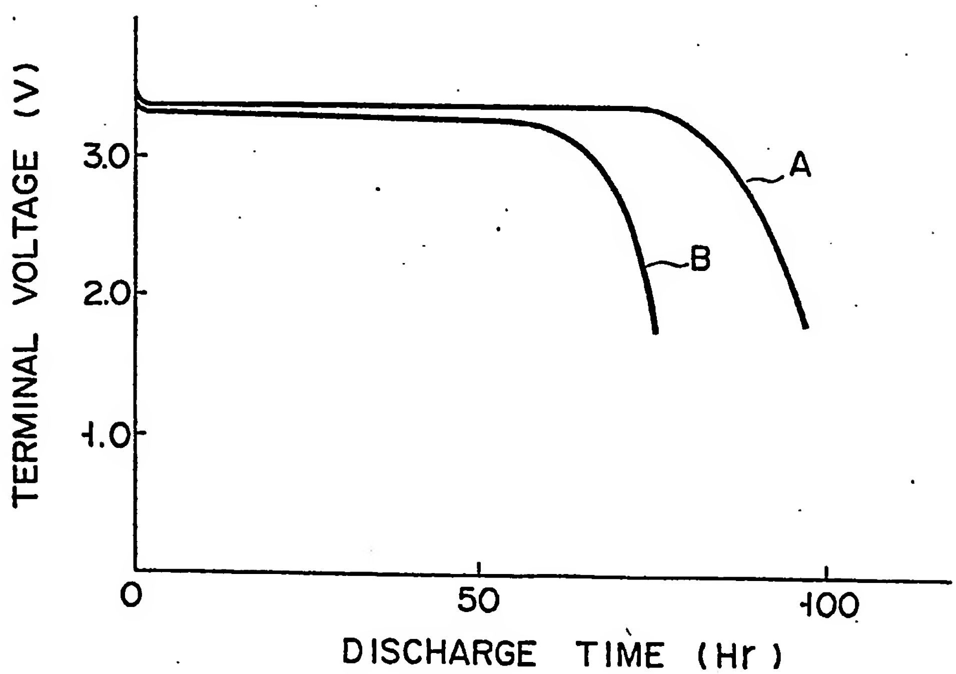
1
7
5

F I G. 2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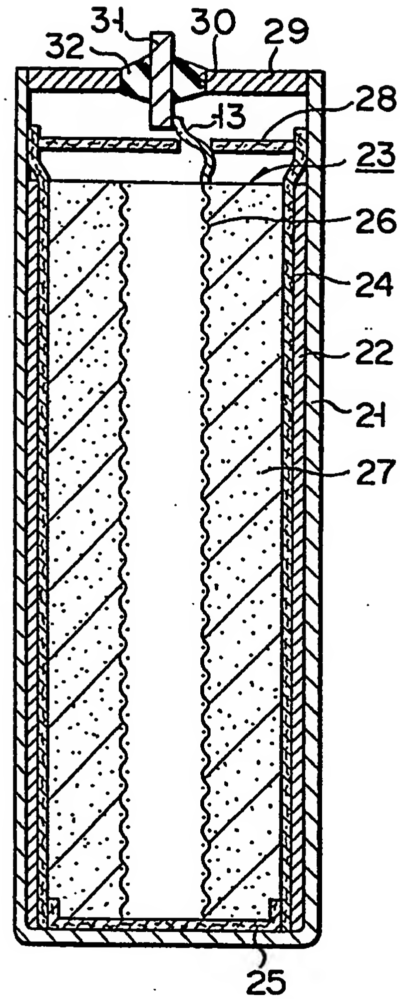
0
50
100
DISCHARGE TIME (Hr)
A
B

F I G. 3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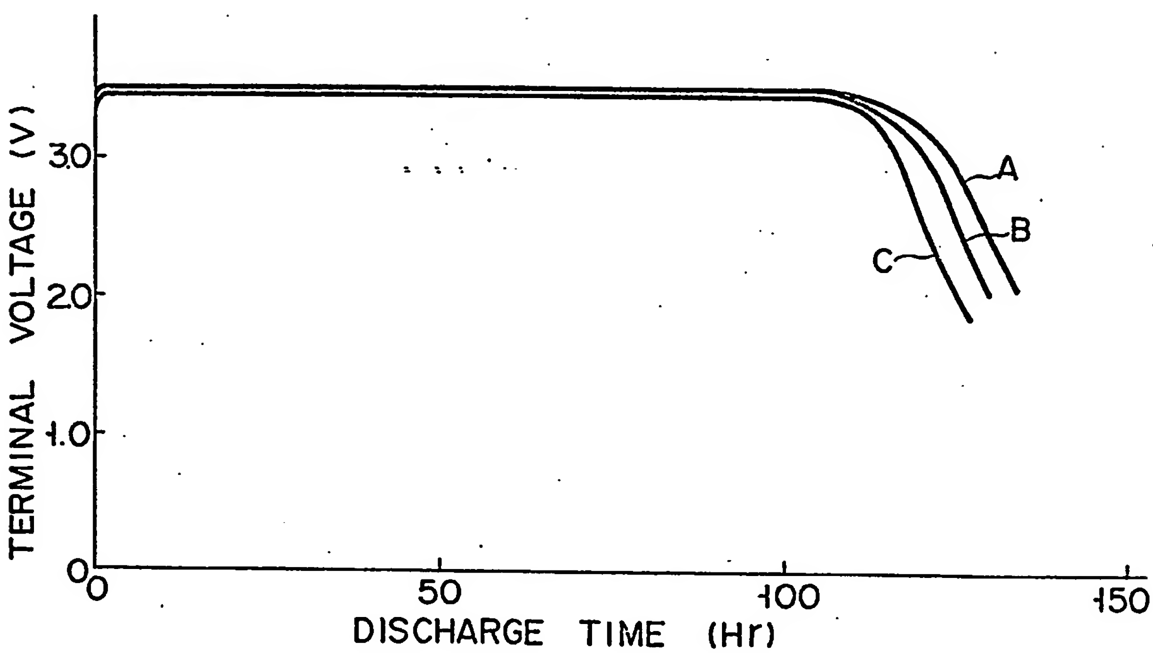
22
21
27
25

F I G. 4


TERMINAL VOLTAGE (V)
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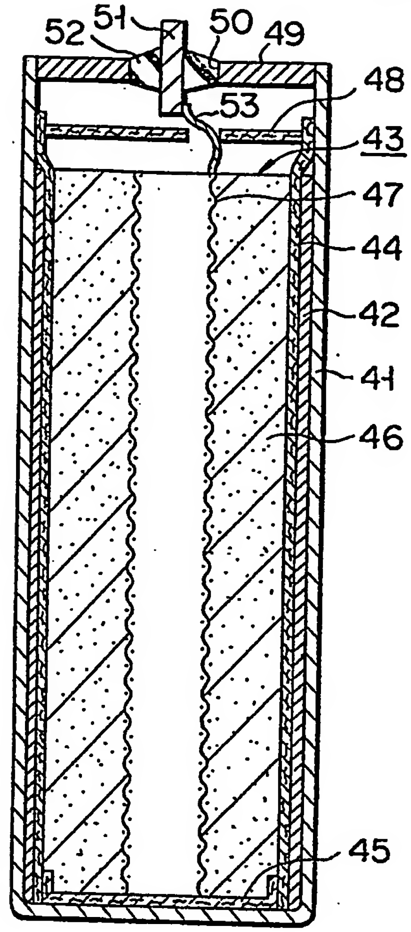
2.0
1.0
0
0
50
100
150
DISCHARGE TIME (Hr)
A
B
C

FIG. 5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49
48
53
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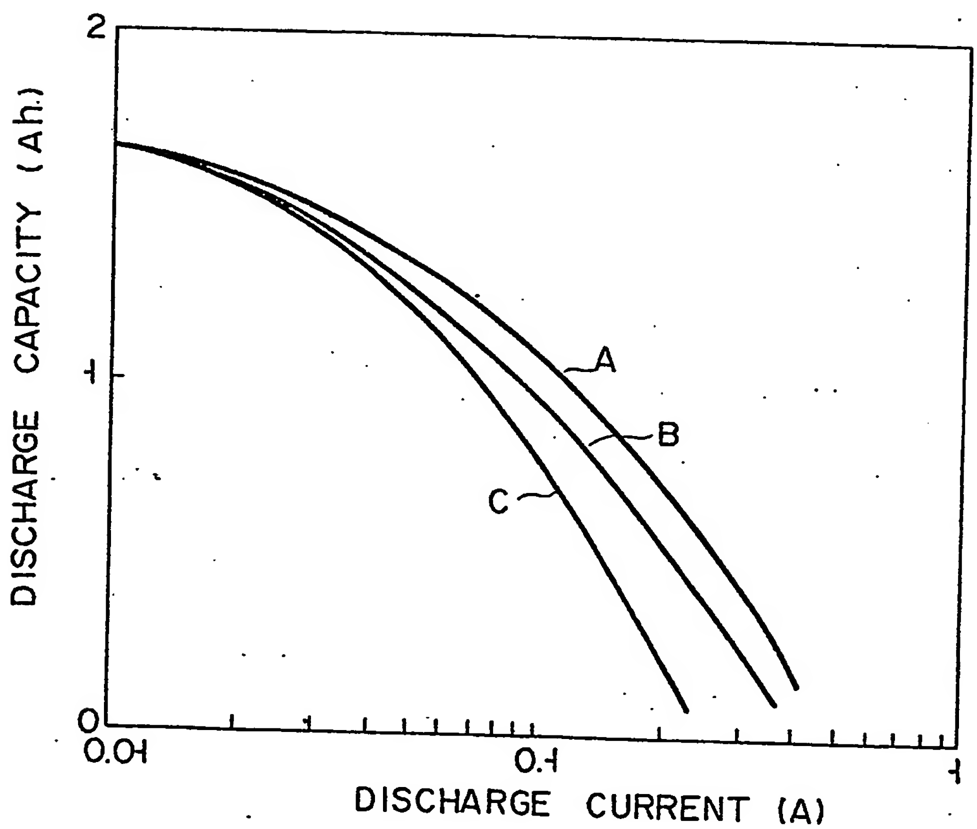
47
44
42
41
46
45

FIG. 6


DISCHARGE CAPACITY (Ah.)
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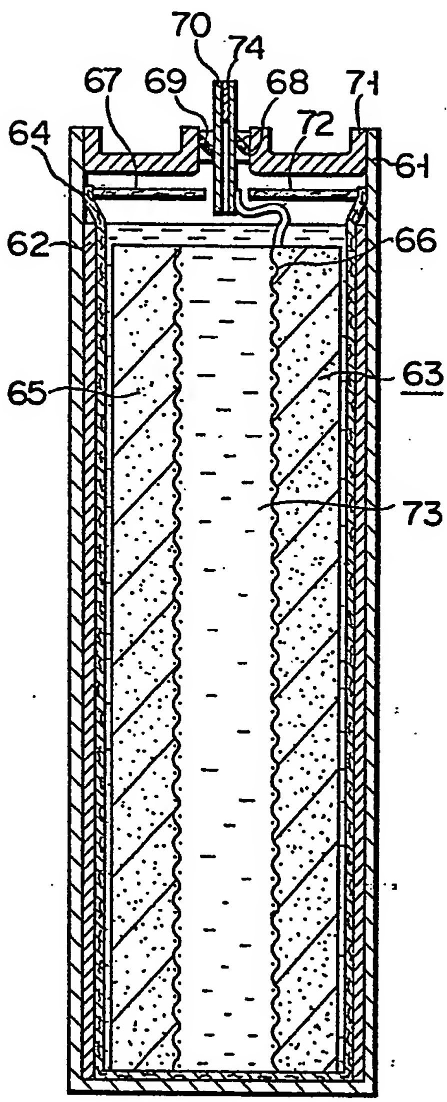
0.01
0.1
1
DISCHARGE CURRENT (A)
A
B
C

F I G. 7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71
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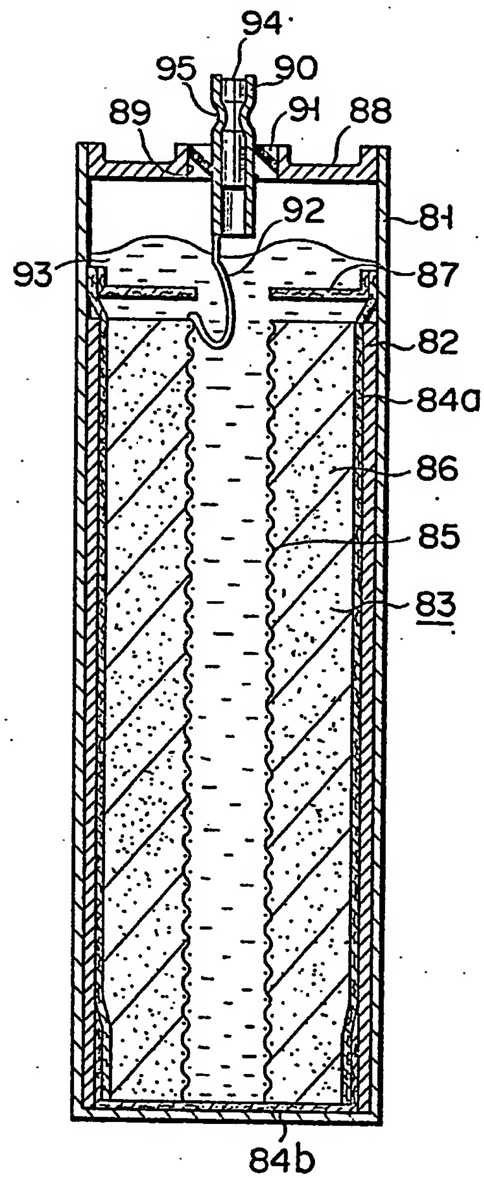
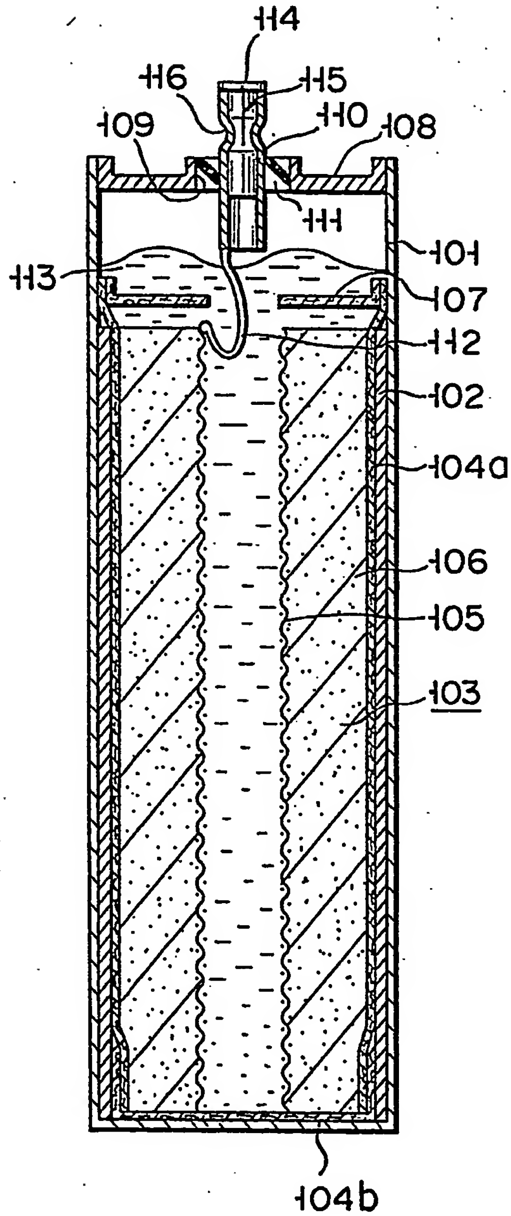
72
61
62
66
65
63
73

F I G. 8


94
95
90
89
91
88
92
81
93
87
82
84a
86
85
83
84b

F I G. 9


114
116
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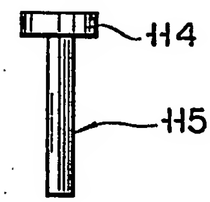
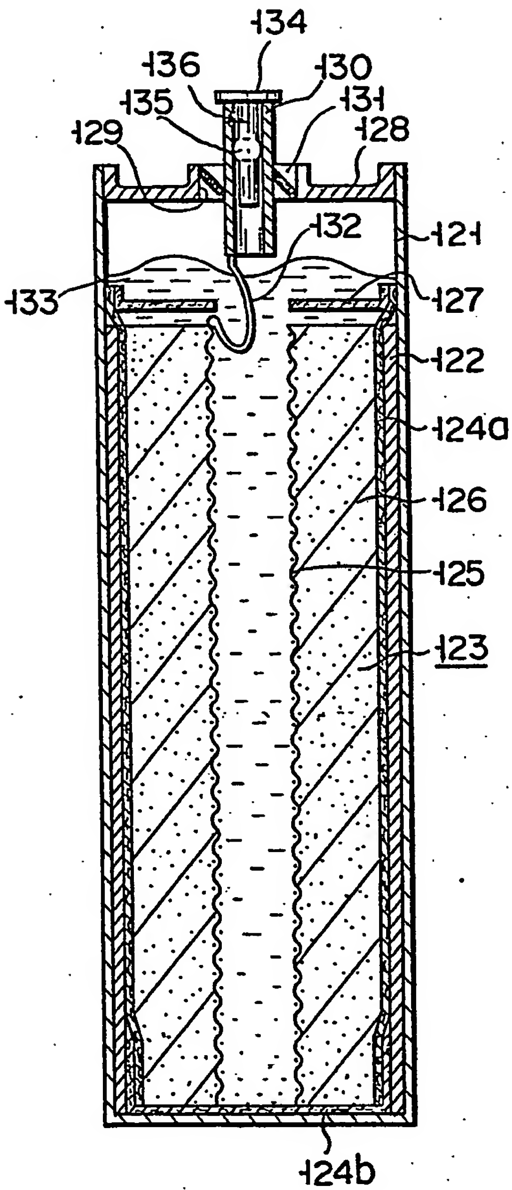
110
109
108
111
101
113
107
112
102
104a
106
105
103
104b

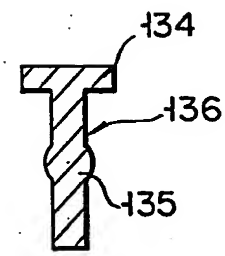
F I G. 10


114
115

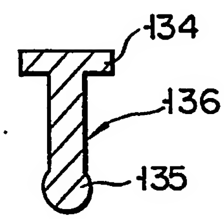
F I G. 11



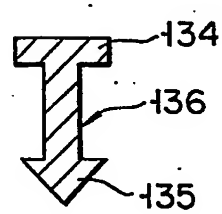
F I G. 12



F I G. 13



F I G. 14



European Patent Office

EUROPEAN SEARCH REPORT

0118657
Application number

EP 84100066.4

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	US - A - 4 093 784 (DRISCOLL) * Claims *	1,3,4	H 01 M 6/14 H 01 M 4/96 H 01 M 4/40
A	US - A - 4 028 138 (DEY) * Fig. 1 *	1,3,6	
A	US - A - 4 042 756 (GOEBEL et al.) * Example 1 *	1,3,4, 6,7,8	
A	US - A - 4 233 372 (BRO et al.) * Fig. 2; claims *	1,6	

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

H 01 M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	17-04-1984	LUX

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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